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The study of the different parameters affecting Liesegang rings formation during the growth of calcium hydrogen phosphate dihydrate crystals

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Abstract . Calcium hydrogen phosphate dihydrate (CHPD) crystals are well known urinary crystals The crystals were grown by the gel technique by diffusing calcium chloride solution into sodium metasilicate gel impregnated by orthophosphoric acid. The formation of Liesegang rings was observed The effect of various parameters such as, the gel pH, the concentration of reactants, the height of the column of supernatant solutions, was studied The gel and its structure were found to be playing an important role in the formation of Liesegang rings

Keywords Gel growth, Liesegang rings, calcium hydrogen phosphate dihydrate, crystals

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1. Introduction

Chemical reactions leading to the formation of precipitates in gels are ideal in sense that the particles of precipitates remain where they are produced and reagents reach each other only by diffusion phenomenon. This study has great importance because chemical reactions in biological media, whether living or dead, and in many geological structures are usually of this type The diffusion of a soluble substance from an aqueous solution into gel, obeys the ordinary diffusion law of Fick. Hedges [1] identified four different types of structures produced by chemical reaction in gels as (1) precipitates of continuous structure, (2) discrete structure, (3) cellular structure and (4) periodic structure. The first interesting study of a periodic structure was made by Liesegang [2]. In many natural and biological phenomena, the Liesegang ring type of structures have been observed; for example, the periodicity in the structure of urinary calculi [3], the concentric rings of beet root [4], the periodic structures found in the geological objects like agates and malachite [5], and the periodic layering in bones [6]. Interestingly, the solid state reaction in the Ag- Ti- Si system produces Liesegang ring type periodic layer formation [7] and Liesegang ring type periodic microstructures have been observed on single crystal surfaces of oxide superconductor $Ba_{0.6}K_{0.4}BiO_3$ [8] as well.

In the present investigation, crystals of calcium hydrogen phosphate dihydrate are grown in silica gel medium. The phenomenon of Liesegang ring is observed. The present authors report the effects of pH of gel, the concentration of supernatant solution, and the height of supernatant solution column on the Liesegang rings.

2. Experimental Technique

The single test-tube diffusion technique was employed for growing calcium hydrogen phosphate crystals in the gel medium. The stock solution of specific gravity 1.08 was prepared by dissolving sodium metasilicate in doubly distilled water at room temperature. This solution was acidified by mixing with orthophosphoric acid in such a way that the desired pH of the mixture could be set. In the present study, pH values of 5.4, 5.6, 5.8, 6.0, 6.2, 6.4, 6.5 and 6.6 were selected. The mixture was transferred into glass test-tubes of 25 mm diameter and 140 mm length. After setting the gel, the supernatant solutions of calcium chloride having molarities from 0.5 M to 2.5 M were poured without disturbing the gel sufaces. Star and needle shape crystals were found to be growing within Liesegang rings.

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3. Results

3.1 Distance of different Liesegang rings from the first ring :

Distance of different Liesegang rings was measured from the first ring from the gel-liquid interface for pH value of 6.0 with different concentrations of supernatant solutions, namely, 0.5M, 1.0M, and 1.5M of calcium chloride solutions. The distance increases rapidly with the number of rings. Figure 1 shows the plots of distance of Liesegang rings from the first ring from the gel-liquid interface *versus* the number of rings.

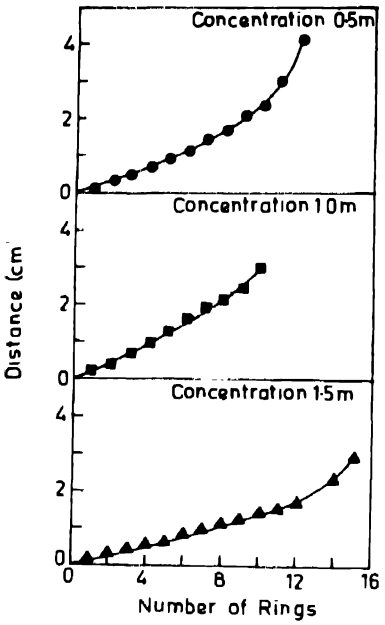

Figure 1. Plots of distance of Liesegang rings from the first ring from the gel-liquid interface *versus* the number of rings for various concentrations of supernatant solutions

3.2 The effect of Gel pH on the Liesegang rings :

Sodium metasilicate solution of 1.08 specific gravity was taken, which was acidified by mixing with orthophosphoric acid of 0.5M concentration in such a way that different pH values, *viz.* 5.4, 5.6, 5.8, 6.0, 6.2, 6.4, 6.5 and 6.6 could be set for different mixtures. The mixtures were poured in different test-tubes. After gelation took place, the solution of calcium chloride having 0.5M concentrations was gently poured. The distance between consecutive Liesegang rings were noted in each test-tubes by travelling microscope of least count 0.01 mm. Figure 2 is the photograph showing the Liesegang rings formed for pH value of 6.0.

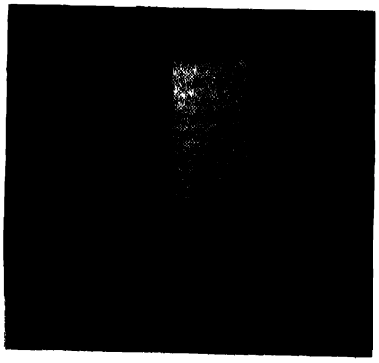

Figure 2. Photograph exhibiting the types of Liesegang rings observed for pH 6.0

It was found that the Liesegang ring formation was observed only for pH range 5.4 to 6.6. The experiment was repeated for 1.0M and 1.5M concentrations of calcium chloride and orthophosphoric acid. Figure 3 shows plots of the distance

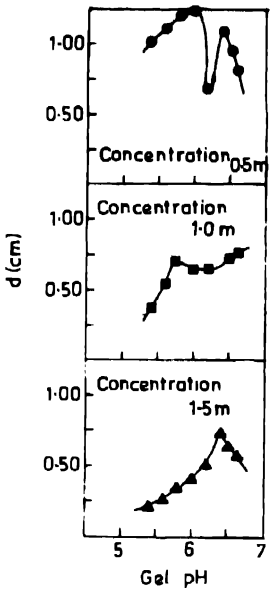

Figure 3. A set of plots of the distance between the last two Liesegang rings (d) *versus* gel pH for different concentrations

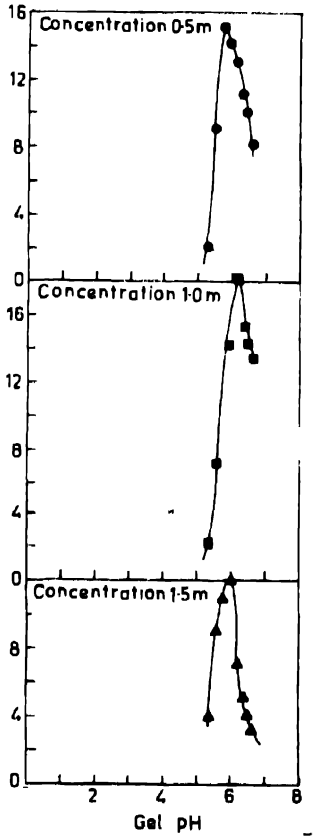

Figure 4. Plots for number of Liesegang rings (N) *versus* gel pH for

between the last two Liesegang rings *versus* gel pH. The rings formed remained unchanged even after one and half years. In the case of 0.5M concentrations, good quality and maximum number of rings were observed at pH of 5.8, whereas for 1.0M concentrations at 6.2 pH and for 1.5M concentrations, at 6.0 pH were obtained. For any specific concentration, the number of Liesegang rings first increases with pH and then decreases after achieving a maximum value. Figure 4 shows plots for number of Liesegang rings *versus* gel pH for 0.5M, 1.0M and 1.5M concentrations.

3.3 The effect of concentration of reactants on the Liesegang rings :

Sodium metasilicate solution of 1.08 specific gravity was used to set the gel. Orthophosphoric acid of concentrations 1.75M, 2.0M, 2.25M and 2.5M were used to mix with sodium metasilicate solution in such an amount that the pH of 6.0 could be set for the mixtures. After gelation took place, calcium chloride solutions of respective molarities from 1.75M to 2.5M were gently poured on the set gels. The number of good quality Liesegang rings formed in each test-tubes were noted. The number of good quality Liesegang rings first increases with molarity of the reactants and thereafter, decreases after achieving the maximum value. Figure 5 is a plot of number of Liesegang rings *versus* the molarity. The Liesegang rings remained unchanged even after one and half year.

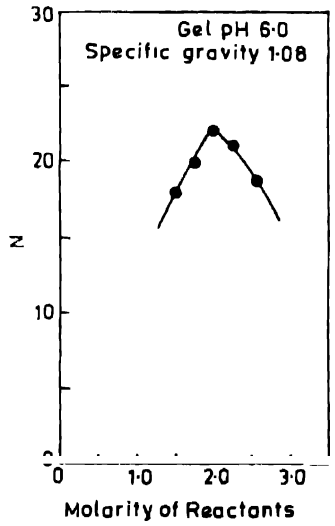

Figure 5. Plot of number of Liesegang rings (N) *versus* molarity of reactants for gel pH 6.0 and specific gravity 1.08

3.4 The effect of concentration of reactants on the distance of Liesegang rings :

Sodium metasilicate solution of 1.08 specific gravity and orthophosphoric acid solutions of 0.5M, 1.0M, 1.5M and 2.0M concentrations were mixed in such a way that pH 6.0 was obtained for the mixtures. After gelation, the supernatant solutions of calcium chloride having the same concentrations were poured on the set gels. The distances between each consecutive ring were measured by travelling microscope. The distances between two consecutive Liesegang rings were found to be decreasing as the concentrations of reactants were increased. Figure 6 is the plot of the distance between the last two Liesegang rings *versus* the concentration.

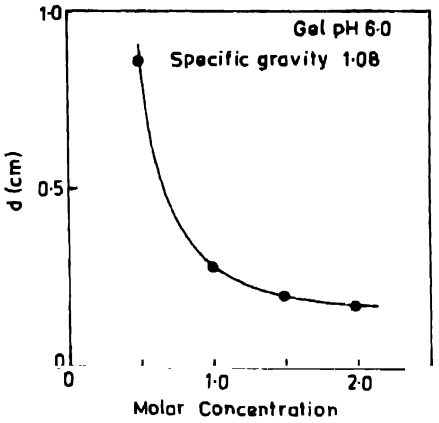

Figure 6. Plot of the distance between the last two Liesegang rings (d) *versus* the concentrations of reactants, for gel pH 6.0 and specific gravity 1.08

3.5 The effect of the height of supernatant solution :

The specific gravity of sodium metasilicate solution was chosen to be 1.08 and the pH of the mixture of sodium metasilicate and 1M orthophosphoric acid was set to 5.8. A supernatant solution containing 1M calcium chloride was poured on the set gels in different test-tubes in the columns of heights 1.5 cm, 3.0 cm, 4.5 cm and 6.0 cm. Liesegang rings were observed and measurements were made by using travelling microscope of least count .01mm. In the present investigation, the number of Liesegang rings formed increased with the height of the column of calcium chloride solution. The number of rings were 14, 17, 18 and 20 for 1.5 cm, 3.0 cm, 4.5 cm and 6.0 cm column heights, respectively. The same experiment was repeated for 0.5M, 1.0M and 1.5M concentrations of calcium chloride and orthophosphoric acid,

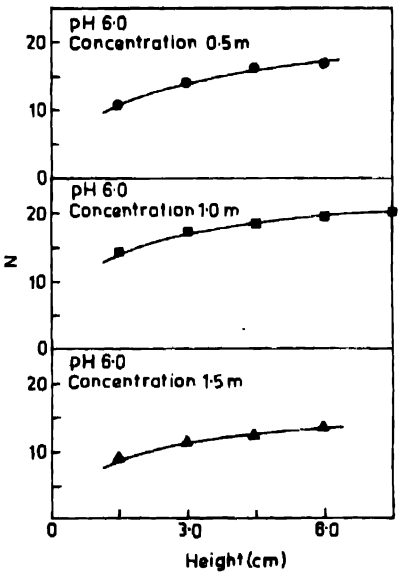

Figure 7. A set of plots of number of Liesegang rings (N) *versus* height of the supernatant solution column at different concentrations.

for pH 6.0. Figure 7 is a set of plots of number of Liesegang rings *versus* height of the supernatant solutions of molarities 0.5M, 1.0M and 1.5M. Figure 8 exhibits a set of plots, drawn for different concentrations, of the distance between last two Liesegang rings and the height of the column of supernatant solutions. Except for 1.5M concentration, the distance between last two rings increases with the column height.

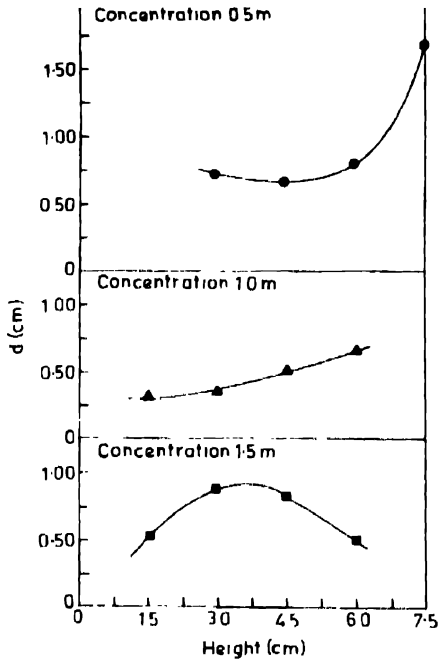

Figure 8. Plots of the distance between last two Liesegang rings (d) *versus* the height of the column of supernatant solution, for different concentrations of reactants

4. Discussion

Many authors have suggested various theories for the Liesegang ring phenomenon. Henisch and Garcia-Ruiz [9] suggested a numerical method to obtain the formation of Liesegang ring on the basis of Fick's diffusion equation for reagents in gel as a function of time. In another study, Henisch and Garcia-Ruiz [10] extended the conditions under which two diffusing reagents could form precipitates either continuous or periodic in a gel media. The periodic nature of Liesegang ring, ring masses, and ring spacing were theoretically calculated. After finding the position of the first precipitates, the local solute concentrations must be decremented, after which the interactions could resume, until a second point was found at which the precipitation conditions were satisfied. A precipitate once formed was assumed to grow until the next precipitation occurred. The precipitates had positions and mass but no explicit thickness, where and when a precipitate was formed and was the outcome of a complex interplay of processes, which depended not only on local concentrations but on the steepness of the supersaturation front and the speed of its advance.

A microscopic approach to the formation of Liesegang patterns, based on a cellular automate model has been presented by Chopard *et al* [11]. Another model suggested by Chernavskii *et al* [12], takes into account of effects of supersaturation competition between nucleation and droplet growth kinetics as well as redistribution of matter between particles of precipitant On the other hand, many authors have incorporated diffusion-based models and theories. A turning type reaction- diffusion model is explored by Brechet and Kirkaldy [13], which can be applicable to Liesegang bands, rings and spirals evolving by precipitation in the environments of an equilibrium solubility product reaction. Diffusion coefficient of barium ions from Liesegang ring formation have been estimated by Dharmaprakash and Mohan Rao [14] using the simple mathematical model based on Kirov model [15]. Moreover, Verghese *et al* [16] estimated the diffusion coefficient in multi component systems forming Liesegang rings. Apart from this, some computer simulation experiments also have been carried out. Buki *et al* [17] studied regular Liesegang structure by means of computer simulation. Also, Buki *et al* [18] studied two dimensional chemical pattern formation in gels by experiments as well as computer simulations.

Influence of various conditions on Liesegang rings are summarized by Hedges [5], which are concentration, effect of light, temperature, reaction medium, the presence of impurities effect of electric field, gravity, tension and age of the gel By and large, in a given system, the ring formation depends on the concentration of both reagents and of the gel, and as a general rule, the distance between the bands decreases with increasing concentration of reagents and gel. The effect of pH on the Liesegang ring formation of lead carbonate crystals is reported by Pillai *et al* [19] in the range of pH from 6.00 to 8.00 at room temperature. Below a pH value of 7, they have found discrete rings, whereas above 7.0 pH value, interconnected rings have been found. Also, the time of formation of the rings is decreased and the number of rings increased with pH They attributed this to the differences in solubility of the crystals formed and structure of the gel at different pH values.

Calcium hydrogen phosphate crystals are well known urinary crystals. Recently, Joshi [20] has reported the influence different additive solutions on the growth of calcium hydrogen phosphate dihydrate crystals and the Liesegang rings formed during the growth. In the present investigation, an attempt is made to study different fundamental parameters affecting the formation of Liesegang rings.

Gels are neither liquid nor solid in nature, it is not a simple three dimensional network; actually, it contains sheet-like structures of varying degrees of surface roughness and porosity forming interconnected cells. The cell walls are ordinarily curved In dense gels, the pores are from 0.1μ to 0.5μ, whereas in low density gel, those are from less than 0.1μ to 4μ. By varying the pH, the gel density and the pore size distribution are altered Therefore, at particular value of pH, the maximum diffusion of reactants is expected, which leads to more periodic precipitation and the maximum number of Liesegang rings are observed. For higher concentrations, the higher numbers of ions are available and this is shifted to higher pH value. More or less, simila

behavior is obtained when the pH and density of gel are kept constant and the concentrations of reagents are increased. There is a particular concentration at which the maximum numbers of rings are observed. As the concentration of reactants increased, for fixed value of pH and gel density, the distance between two consecutive Liesegang rings is found to be decreasing because of more nutrients are available for diffusion and rapid periodic precipitations are occurring.

The effect of height of the supernatant solution column indicates that for fixed values of pH and gel density, the number of Liesegang rings increases with the column height. This is due to more nutrients available and the hydrostatic pressure of the solution column facilitates the diffusion of reactants, which leads to more periodic precipitations. However, for fixed pH and gel density, the distance between last two Liesegang rings increases with the height of the supernatant solution column; but in the case of 1.5M molar concentrations, a maximum value is obtained and thereafter the distance decreases with the height. This may be due to the nature of gel influencing at higher concentrations. This type of behavior is already discussed earlier in the case of the effect of pH and concentration of reactants on Liesegang rings. The present study indicates that the gel has important role to play in the formation of Liesegang rings. The gel structure and its nature are very important.

5. Conclusions

The growth of urinary type calcium hydrogen phosphate dihydrate crystals, takes place within the Liesegang rings. The gel and its structure play an important role in the formation of Liesegang rings. By changing the pH, the gel density and the pore size distribution are varied. Therefore, at particular value of pH, the maximum diffusion of reactants is observed, which leads to more periodic precipitations and hence the maximum number of Liesegang rings. The similar behavior is noticed when the pH and density of gel are kept constant and the concentrations of reactants are increased.

The effect of height of the supernatant solution column suggests that for fixed values of pH and gel density, the number of Liesegang rings increases with the column height which is due to more nutrients available and the hydrostatic pressure of the solution column to facilitate the diffusion of reactants.

The formation of Liesegang rings and their periodicity are according to the theory suggested by Henisch and Garcia-Ruiz [9, 10].

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